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We reported evidence of quasi-continuous optical gain in CdS quantum dots (QDs) fabricated by the sol-gel process and embedded in glass.¹ The gain spectra were obtained using the pump and probe technique and nanosecond (quasi resonant) excitation at 11 K. The dots were in the intermediate quantum-confinement regime and the concentration of CdS is relatively high. The gain, which is spectrally broad, develops on the low energy side of the absorption band edge. The reason why the gain region is broad is not only the size distribution of the dots, but also the nature of the gain, which originates from the recombination of several excited levels between two and one electron-hole pairs states (i.e., biexciton to exciton). The maximum measured gain reaches 200 cm^{-1} at 11 K and 17 cm^{-1} at 170 K.

Three-dimensionally quantum-confined semiconductors are attractive because of the predicted enhanced optical properties with increasing confinement. Semiconductor QDs have been investigated extensively² but have not shown superior emission properties. One known problem is the reduced radiative efficiency with decreasing dots as a result of surface recombination. Especially for QDs in glass, limitations are the large size in distribution of the dots, the presence of trap states (such as vacancies, substitutional defects and dangling bonds), the observed photodarkening, and the low density of microcrystallites (active material) in the glass matrix.

Semiconductor crystallites in glass have a number of advantages including the relatively easy growth of QDs of difference II-VI semiconductors by heat treatment and the possibility of fabricating low loss waveguides with ion exchange in the high quality glass matrix. The quality of our QDs has been improved with the use of the sol-gel synthesis³ high dot density, dot sizes much smaller than the bulk exciton Bohr radius α_{Bohr} , with more uniform size distribution and an almost complete elimination of the photodarkening effect.⁴

Femtosecond dynamics of optical gain in strongly confined CdSe QDs has recently been studied using femtosecond (fs) optical excitation.⁵ Gain in the weak confinement regime for CuCl crystallites in glass has also been studied at 77 K.⁶

We reported measurement of the gain spectra of sol-gel derived CdS QD glasses in the intermediate confinement regime and compared the results with the calculated gain for a quasi zero-dimensional-hole system, accounting for one and two electron-hole pair states.¹ Using the variable-stripe-length method, we analyzed the temperature dependence of the gain between 11 K and 170 K.

The CdS nanocrystallites we investigated were fabricated by the sol-gel process:³ 5.6 wt. % CdS nanocrystallites were embedded in a fully dense $4\text{Na}_2\text{O}-15\text{B}_2\text{O}_3-80\text{SiO}_2$ (mol %) glass after heating at 590C. The transmission electron micrograph (TEM) in Figure 1(a) shows that the average dot radius R was 2.8 nm with a distribution of σ (standard

deviation) = 1.0. The average radius R of the dots was on the order of the bulk exciton Bohr radius. Figure 1 (b) shows a typical image of these nanocrystallites with high-resolution transmission electron microscope (HRTEM: Topcon 002B, 200 kV). These crystallites of $R \approx 2.5$ nm (graphitized carbon internal standard) are both oriented perpendicularly to the (101) reflection plane. The electron and x-ray diffraction patterns of our sample show that the crystallites are of hexagonal symmetry.



Figure 1. (a) TEM micrograph and (b) HRTEM micrograph of the 5.6 wt % CdS-doped sodium borosilicate glass.

The glass sample was polished to a thickness of 17 ± 2 μm and held in a cryostat at $T = 11$ K for optical characterization. Differential transmission spectra (DTS) and absorption spectra have been measured in the common pump and probe technique, with 3 ns duration pump pulses at 10 Hz repetition rate. The probe beam, originating from the luminescence of a dye cell, had an 8 ns pulse duration and was cross polarized with respect to the pump to reduce the scattered light. The time delay between the pump and the probe pulses was less than 1 ns.

Figure 2(a) shows the absorption spectra for different pump intensities. A bleaching of the absorption spectrum is observed as the excitation intensity is increased. The position of the maximum (around 465 nm) does not change when we vary the pump wavelength, even for low excitation intensity. This can be interpreted as a low inhomogeneous broadening,⁷ giving another indication of the relatively narrow size distribution of the QDs. A broad gain region (negative absorption), ranging from ≈ 470 nm to ≈ 540 nm, is observed for the highest pump intensity. These results are in agreement with the results of Dneprovskii et al.,⁸ who have observed gain in CdSe QDs in the intermediate confinement regime. The maximum gain reaches about 200 cm^{-1} at 493 nm for an excitation intensity $I_0 = 570 \text{ kW/cm}^2$. The rapid oscillations in the gain region are Fabry-Perot interferences, whose period corresponds to the sample thickness. The pump wavelengths are 455 and 440 nm, respectively, for the two input intensities I_{exc} , as indicated by the sharp scattering signals. The comparison with the linear absorption spectrum (dashed curve) shows that the gain develops on the low energy side of the

adsorption band edge and extends well below the band edge. This behavior is expected of the gain involving two electron-hole (eh) pair (biexciton) recombination.⁹

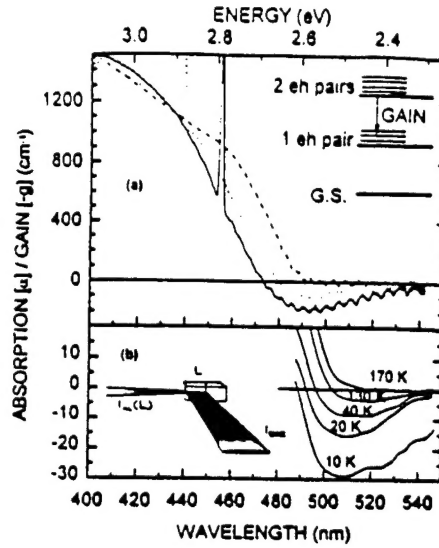


Figure 2. (a) Absorption (gain) spectra of CdS QDs measured at 11 K for different pump excitation intensities I_{exc} . The pump wavelength is 455 nm for the solid curve ($I_{exc} = I_0$) and 440 nm for the dotted curve ($I_{exc} = I_0/7$), with $I_0 = 570 \text{ kW/cm}^2$. The dashed curve is the linear absorption spectrum. The inset shows a scheme of the energy levels considered for the model calculations: the ground state and the one and two electron-hole pair levels with their excited states, and one of the recombinations which provide the optical gain. (b) Temperature dependence of the gain between 10 K and 170 K. The spectra were measured with the variable-stripe-length method (see the inset), with an excitation intensity $I_{exc} = 3I_0$ at 355 nm.

The temperature dependence of the gain between 11 K and 170 K is presented in Figure 2(b). The variable stripe-length method was used to measure the gain spectra.¹⁰ The third harmonic of the Nd:YAG laser was focused on to the sample by using a cylindrical lens to form a narrow rectangular stripe, 0.05–2 mm long and about 20 μm wide. The emitted light (i.e., amplified luminescence I_a) was collected from the edge of the sample in the direction of the strip, as shown in the insert in Figure 2(b). That method allowed us to reproduce the gain spectra of Figure 2 (a) (solid line) when we pumped with $I_{\text{exc}} \approx 8I_0$ at 355 nm. As expected, the gain decreases with increasing temperature, rapidly at the beginning (it is already two times smaller at 20 K), and it disappears around 170 K. By increasing the excitation intensity to 10 MW/cm², the maximum gain at 170 K was 17 cm⁻¹.

We also reported on results obtained in areas of: fabrication of waveguides in CdS quantum dot sol-gels and on the study of pulse propagation effects and the fabrication of ion-exchanged waveguides in glass to be used as substrates for quantum dot sol-gel integrated devices

We fabricated waveguides in CdS quantum dot sol-gels and studied pulse propagation effects. Pulse propagation experiments were performed using a femtosecond laser system tuned near a two-photon resonance while being well below the lowest one-photon transitions. The samples were single-mode waveguides of CdS doped borosilicate sol-gel glass, and were prepared with a CdS concentration of 6.2 wt%. The waveguides were fabricated by potassium-sodium ion exchange through 3 μm openings in an aluminum mask. The radius of the dots was determined as $R = (1.5 \pm 0.45)$ nm, the mean radius being half a Bohr radius, and the linear absorption spectrum showed the lowest one-photon transition as a shoulder appearing at (2.7 eV) 460 nm. An amplified CPM dye laser system tuned to 1.84 eV (675 nm), with 80 fs typical pulse width, was end-fired onto the sample. Single beam optical transmission measurements were performed on a 3 mm long CdS doped waveguide for varying input pulse energy. A reduction in transmission with increasing input energy was observed, indicating a two-photon absorption (TPA) process. The temporal and spectral changes of the femtosecond pulses after propagation in the waveguide were explained by a pulse propagation model incorporating a near resonant two-photon transition. For our numerical simulations we have used a two-photon two-level model for the QDs, where we have neglected the Stark effect and assumed small transfer of population. The resulting third-order nonlinear polarization was used in the propagation equation, and these were then solved numerically for incident Gaussian pulses of 80 fs duration, with a two-photon resonance centered at 3.4 eV and linewidth 0.16 eV. Good agreement between the experimental observations and the two-photon two-level model was obtained. The TPA was not accompanied by visible flat topping of the transmitted pulses, but the pulse spectrum clearly revealed the dynamical nature of the nonlinear interaction.

We have developed an ion-exchange process for fabrication of single mode channel waveguides in glass. Our process is sketched in Fig. 3. The glass surface is covered by a 200 nm thick sputter-deposited Ti mask. Narrow openings ($\sim 2\text{--}5$ μm) are photolithographically patterned in Ti to locally control the ion exchange. The waveguides

are formed just beneath the glass surface by immersing the glass at a temperature of 300 °C in an AgNO_3 salt melt for about 20 min. After the ion exchange the Ti mask is removed and the end facets of the glass chip are polished.

We have fabricated our waveguides in a high quality borosilicate glass BGG31 provided by our collaborator IOT (Germany). We have characterized the waveguides at 1.55 μm wavelength by coupling light from a laser diode in the waveguides and imaging the output to an IR-camera. We can now reproducibly produce low loss single-mode channel waveguides for communications wavelengths.

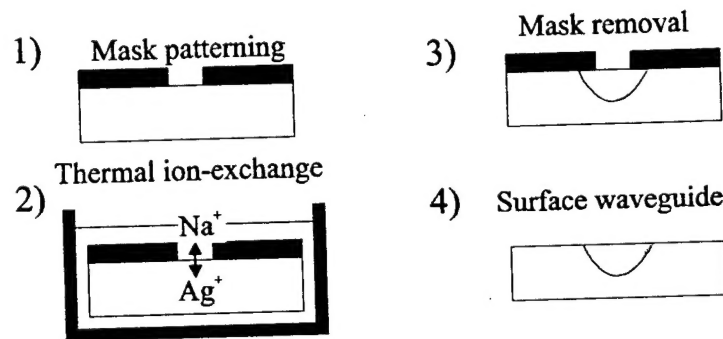


Fig. 3: Waveguide fabrication process by ion exchange.

Our approach in developing non-linear PbS-doped glass waveguides is following: We fabricate the channel waveguides in the high quality BGG31 glass rather than employing the PbS-doped sol-gel glass as a substrate. Then the PbS-doped sol-gel thin film is dip-coated (UCLA) on the waveguide chip. This allows us to combine the excellent waveguiding properties of the ion-exchanged waveguides in BGG31 and the non-linear properties of the PbS thin film. There is no need to form waveguides on the PbS-doped glass since the lateral confinement is provided by the "passive" glass waveguide. We have also modeled the structure and shown that a great deal of the optical power can be guided in the active overlayer if the refractive index and thickness of the active thin film are chosen properly. An example of our modeling results is shown in Fig. 4. It illustrates that the mode is well confined, also laterally, in the $0.5\text{ }\mu\text{m}$ thick overlayer.

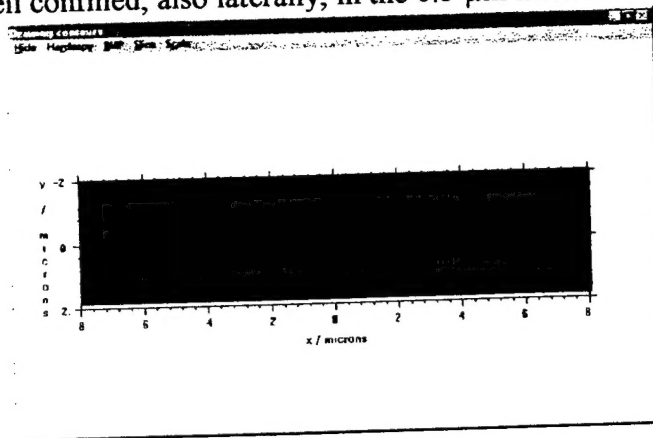


Fig. 4: Calculated optical mode intensity distribution in an ion-exchanged glass waveguide with sol-gel thin film glass as an overlayer. The substrate-thin film interface is at $y=0$.

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